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Supplemental Quality Assurance Criteria for High-Resolution Gas Chromatography/High-Resolution Mass Spectrometric Determination of 2,3,7,8-Tetrachlorodibenzo-p-dioxin in Biological Tissue

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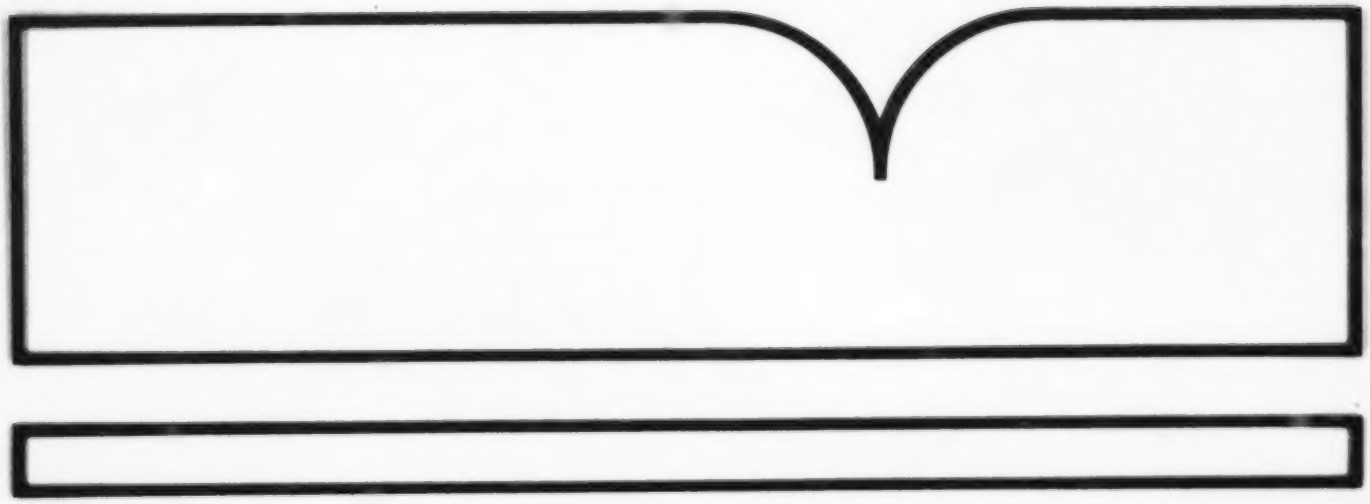

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16. ABSTRACT

An analytical technique has been developed to demonstrate both mass spectral and gas chromatographic resolution during each HRGC/HRMS-M5D determination of TCDD. The technique uses $^{13}C_6$ 1,2,3,4-TCDD and $^{37}Cl_4$ 2,3,7,8-TCDD to demonstrate the resolution. A technique has also been developed to measure the minimum level of detection of TCDD in each sample.

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Supplemental Quality Assurance Criteria for High-Resolution Gas Chromatography/High-Resolution Mass Spectrometric Determination of 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin in Biological Tissue

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During the past 2 years our laboratories have been responsible for the analysis of nearly 2000 fish tissue samples for part-per-trillion levels of 2,3,7,8-tetrachlorodibenzo-*p*-dioxins (2,3,7,8-TCDD) through both our in-house toxicology studies and the U.S. EPA National Dioxin Study. We wish to share several ideas resulting from this work that can be incorporated into an analytical protocol and quality assurance plan. We do not, however, intend to recommend any specific analytical methodology or quality assurance criteria.

Three areas of concern in 2,3,7,8-TCDD analysis are (1) mass resolution, (2) chromatographic isomer specificity, and (3) minimum level of detection. Currently practiced analytical procedures and quality assurance plans describe only techniques to establish or verify instrumental parameters prior to or after TCDD analyses (*1*). These methods primarily utilize [$^{13}C_{12}$]2,3,7,8-TCDD and [$^{37}Cl_4$]2,3,7,8-TCDD to conduct an isotope dilution mass spectrometry experiment and the 22 TCDD isomers to establish gas chromatographic isomer specificity. Mass spectrometer resolution is most often established by using a reference mixture such as perfluorokerosene. We have had synthesized [$^{13}C_6$]1,2,3,4-TCDD (Cambridge Isotope) and have purchased 1,2,3,4-TCDD (Supelco). The use of these additional standards, along with the others previously mentioned, allows for the development of quality assurance criteria for the measurement of mass resolution, chromatographic resolution, and minimum level of detection during each TCDD GC/MS analyses. The method developed for the cleanup of biological tissue samples is capable of isolating many polychlorinated dibenzo-*p*-dioxins (PCDDs) in addition to 2,3,7,8-TCDD (*2*).

1. Mass Resolution. The requirement for mass resolution is dependent upon resolution of 2,3,7,8-TCDD from other biological and anthropogenic chemicals during sample preparation. Generally the resolution of the mass spectrometer is set in a static mode, while generation of data occurs during a dynamic multiple ion detection (MID) scanning mode. The resolution at which the mass spectrometer is operating can be determined by peak width measurements for GC/MS systems that are capable of generating a high-resolution mass peak profile. We have found that the performance of a mass spectrometer that monitors a defined mass window can be verified during each analysis by monitoring for the two internal standards [$^{37}Cl_4$]2,3,7,8-TCDD and [$^{13}C_6$]1,2,3,4-TCDD, at m/z 327.8847 ($M^+\cdot$) and 327.9137 ($(M + 2)^+\cdot$), respectively. A mass resolution of greater than 11 300 is required to separate these two ions. Since these two compounds are chromatographically separated, a measure of the amount of non-mass-resolved [$^{13}C_6$]1,2,3,4-TCDD ion current at the [$^{37}Cl_4$]2,3,7,8-TCDD ion GC retention time (and/or vice versa) vs. mass resolution may be used to calibrate mass resolution up to 11 300. Mass resolution during each TCDD analysis may then be verified by demonstrating that the amount of non-mass-resolved ion current measured at the mass resolution chosen for the analyses does not exceed an acceptable quality assurance requirement. Since the "calibration curve" for any specific GC/MS/computer system may not be linear, careful measurement at the limits of quality assurance requirements are desirable. Figure 1 demonstrates "peak overlap" at mass resolution of 5000 and 10 000 on our Finnigan-Mat 8230 system.

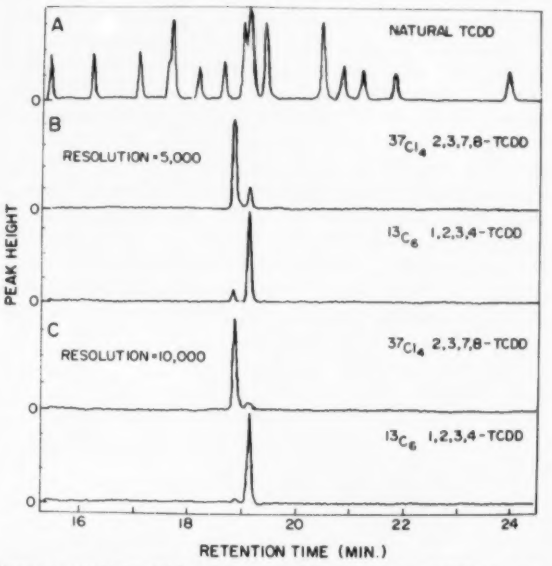

Figure 1. (A) Selected ion current profile for 21 natural TCDD isomers (m/z 321.8936) on a 60-m SP2340 capillary column. (B and C) Selected ion current profile for [$^{37}Cl_4$]2,3,7,8-TCDD (m/z 327.8847) and [$^{13}C_6$]1,2,3,4-TCDD (m/z 327.9137) at mass resolution of 5000 and 10 000, respectively.

2. Chromatographic Isomer Specificity. The need to demonstrate chromatographic isomer specificity is a requirement for the confirmation of 2,3,7,8-TCDD. This involves two steps: first, one must establish isomer specificity on the GG column selected for the analyses, and second, one must demonstrate that isomer specificity is maintained throughout the analyses set. We have found that both of these requirements can be verified by using a standard solution containing [$^{37}Cl_4$]2,3,7,8-TCDD, [$^{13}C_6$]1,2,3,4-TCDD, and 21 natural TCDD isomers, excluding 2,3,7,8-TCDD. This method assumes that if the performance of the column deteriorates, chromatography of all the TCDDs will be affected and loss of resolution can be detected by measuring the resolution of only two TCDDs. This is accomplished by first establishing that the retention time for the 2,3,7,8-TCDD isomer, as monitored by [$^{37}Cl_4$]2,3,7,8-TCDD, is sufficiently free from peak overlap due to the other natural TCDD isomers. The resolution of [$^{13}C_6$]1,2,3,4-TCDD and [$^{37}Cl_4$]2,3,7,8-TCDD

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under these chromatographic conditions may then be calculated. Since each sample contains both of these internal standards, chromatographic resolution may be evaluated for each GC/MS TCDD analyses to ensure that quality assurance requirements for chromatographic isomer specificity have not been exceeded. This is also demonstrated in Figure 1.

3. Minimum Level of Detection. Verification of the minimum level of detection (MLD), especially for samples below detection limit (ND), is a complex problem. Reanalysis of every ND after spiking with the analyte at or just above MLD is inefficient and costly. This method, however, must be used at least on a subset of NDs to establish credibility for reporting MLD. Verification of MLD for each sample is certainly an essential part of a monitoring study; however, alternative techniques each have positive and negative points to consider. One solution would be to spike each sample with an additional labeled analyte, such as [$^{13}C_{12}$]2,3,7,8-TCDD. Although this technique would provide an analysis for the "proper" compound, i.e., 2,3,7,8-substituted isomer, one would have to monitor masses other than for natural TCDD. If an alternative natural TCDD were used, correct masses could be used but they must be monitored at a non-2,3,7,8-TCDD GC retention time. We have chosen the second alternative, and spike each sample with natural 1,2,3,4-TCDD at 5.0 times the target MLD and monitor for TCDD masses through an area containing the retention time window for both 1,2,3,4-TCDD and 2,3,7,8-TCDD. We have found this very beneficial for establishing that the sample preparation methodology and GC/MS operating parameters will allow for the quantification of a natural TCDD near MLD that will meet signal to noise (S/N) and ion ratio quality assurance criteria (*3*). However, because fish uniquely bioaccumulate only 2,3,7,8-TCDD of all of the 22 TCDD isomers (*2*), this technique will work for fish (or most other biological tissues), but it may not work for other matrices where all 22 TCDD isomers can potentially be found at high levels.

4. Additional Considerations. Another technique we now use for high-resolution mass spectrometric analysis of 2,3,7,8-TCDD is to monitor the molecular ion of diiodobenzene (m/z 329.8399) as a lock mass ion in place of one of the ions from perfluorokerosene. We have observed an overall reduction in base-line noise for all channels and an increase in S/N of 2–3 times. We believe this is caused by having fewer stray ions in the analyzer, which can create background signals and increase instrumental noise.

Registry No. TCDD, 1746-01-6.

LITERATURE CITED

(1) Tiernan, T. O. In *Chlorinated Dioxins and Dibenzofurans in the Total Environment*; Choudhary, G., Keith, L. H., Rappe, C., Eds.; Butterworth: Boston, MA, 1983; Chapter 13.

(2) Kuehl, D. W.; Cook, P. M.; Batterman, A. R.; Lothenback, D. B.; Butterworth, B. C.; Johnson, D. L. *Chemosphere* **1985**, *14*(5), 427.

(3) *Analytical Procedures and Quality Assurance Plan: National Dioxin Strategy*; U.S. Environmental Protection Agency, EPA/600/3-85-019, 1985.

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